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Michael A. Reshchikov
Virginia Commonwealth University, mreshchi@vcu.edu

P. Visconti
Virginia Commonwealth University

Hadis Morkoç
Virginia Commonwealth University, hmorkoc@vcu.edu

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Blue photoluminescence activated by surface states in GaN grown by molecular beam epitaxy

M. A. Reshchikov,[a] P. Visconti,[b] and H. Morkoç
Department of Electrical Engineering and Physics Department, Virginia Commonwealth University, Richmond, Virginia 23284

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We have studied the broad blue band, which emerges in the photoluminescence (PL) spectrum of *c*-plane GaN layers after etching in hot H_3PO_4 and subsequent exposure to air. This band exhibited a 100 meV blueshift with increasing excitation intensity and a thermal quenching with activation energies of 12 and 100 meV. These observations led us to suggest that surface states may be formed on etched surfaces and cause bandbending, which leads to a shift in transition energy with excitation. The blue PL is related to transitions from the shallow donors filled with nonequilibrium electrons to the surface states, which capture the photogenerated holes. The observed irreversible bleaching of the blue luminescence may be attributed to the metastable nature of the surface states or to the oxygen desorption. © *2001 American Institute of Physics.* [DOI: 10.1063/1.1338496]

Gallium nitride, related nitride semiconductors, and their alloys became an important class of materials widely used in optoelectronic and high-temperature and high-power devices.[1,2] Fabrication of these devices often involves treatment of the semiconductor surface with acids. Dry etching, commonly used for nitride semiconductors, is known to introduce damage, while wet etching is slow in developing because of the high chemical stability of nitrides.[3] Despite notable progress in controlled etching of GaN and other nitrides, very little is known about the surface states in as-grown and etched GaN and how they affect optical and electrical properties of the material. Photoluminescence (PL) is a powerful method for studying defects in semiconductors. Excitation light with above-band-gap-energy photons is absorbed in a very thin surface layer. Consequently, the contribution of surface states to PL may be quite large since the diffusion lengths are small. A recent study of the GaN surface by scanning-tunneling-microscope-induced luminescence demonstrated that threading dislocations are nonradiative defects.[4] Variations in PL from GaN related to dry, wet, and photoenhanced wet etching have been reported recently.[5–8] These were explained by a competition between different channels of recombination due to variation of defect concentration in the bulk near-surface layer caused by etching. In particular, Brown *et al.*[5] attributed the 3.0 eV blue emission, which enhanced considerably after reactive-ion etching, to some metastable defect closely connected to the yellow luminescence since the bleaching of the blue transition accompanied the emergence of the yellow.

It is well known that exposure of GaAs to oxygen/air results in formation of excess As, Ga_2O_3, and As_2O_3 on the surface and causes many gap states that essentially pin the surface Fermi level.[9,10] Therefore, a plethora of surface treatments have been used to unpin the Fermi level in an effort to improve device performance.[11] Although most recombination processes involving surface states are believed to be nonradiative, optically active recombination centers related to the surface have been previously reported in InP (Ref. 12) and porous silicon.[13,14]

In this letter, we present results of an optical study of undoped GaN layers treated in acid. We have found that the surface condition affects the optical properties of GaN and may enhance radiative recombination.

Unintentionally doped GaN layers were grown by molecular-beam epitaxy (MBE) on the *c*-plane of sapphire substrates. The samples were highly resistive, as indicated by room-temperature Hall measurements. The PL measurements were carried out in the temperature range of 10–300 K with a continuous wave He–Cd laser (325 nm). The excitation density was varied over a range of 10^{-4}–100 W/cm^2. The samples for the study were etched in H_3PO_4 at 160 °C for 0.5–10 min and the effect of etching on the sample surface was examined by PL and atomic-force microscopy (AFM).

We have studied the effect of wet etching on PL for a large set of undoped GaN samples grown by MBE with rf plasma or ammonia as a source of nitrogen. All except a few samples demonstrated the following phenomenon: while the GaN etching was negligible, as was confirmed by the AFM study of the as-grown and etched surfaces, a new PL band in the blue range appeared in the low-temperature PL spectrum. Moreover, the intensity of the blue band gradually increased with the time of exposure of the sample to air after the etching. When the air exposure in freshly etched samples is limited to under a minute, the PL spectrum is similar to that for the as-grown samples.

In samples grown by rf MBE at low substrate temperatures, the band-edge emission is weak and the broad blue band dominates the spectrum after etching (Fig. 1). The integrated PL intensity increased in one of the samples ten times and the blue band quantum efficiency amounted to 0.2% after etching and subsequent exposure to air for several hours. In different samples the contribution of the blue band was quite different. While in most of the samples it repre-

[a]Electronic mail: mreshchi@saturn.vcu.edu
[b]Also with: Istituto per lo Studio di Nuovi Materiali per l'Elettronica, CNR, Via Arnesano, 73100, Lecce, Italy.

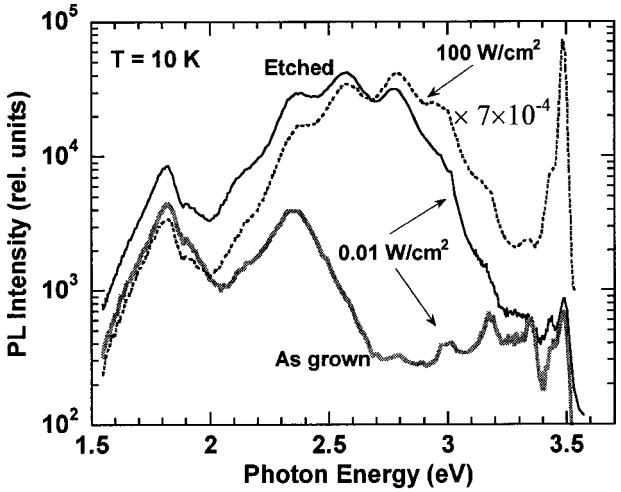

FIG. 1. PL spectrum of the rf-MBE grown sample before etching and after etching in H_3PO_4 at 160 °C for 2 min with subsequent exposure to air for several hours. Oscillations in the spectrum with a period of about 0.2 eV are due to the interference effect. The blue band blueshifts about 100 meV with increasing excitation density.

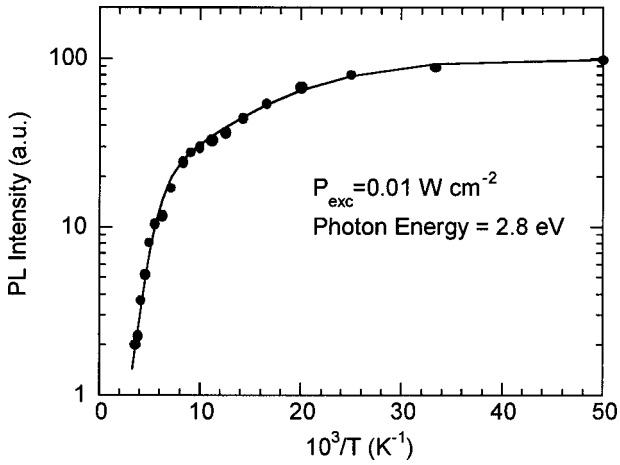

FIG. 3. Temperature dependence of the blue-band intensity (at 2.8 eV) under an excitation density of 0.01 W/cm^2. Points are experimental and the curve is a fit by the equation $I^{PL}=I_0^{PL}[1+A_1\exp(-E_1/kT)+A_2\exp(-E_2/kT)]^{-1}$ with parameters: $A_1=9$, $A_2=3000$, $E_1=12$ meV, $E_2=100$ meV, and $I_0^{PL}=100$.

sented a broadband with a maximum at about 2.6 eV and a full width at half maximum of the order of 0.5 eV, sometimes the PL, activated by etching extended up to 3.3 eV.

To gain some insight, we have studied the effect of excitation intensity on the blue band in the sample where it is the largest contributor. With increasing excitation density from 10^{-2} to 100 W/cm^2, the blue band gradually blueshifted about 100 meV, while the shape and width remained unchanged, as shown in Fig. 1. At high excitation intensities the blue band intensity saturates, whereas the exciton-related peak intensity at about 3.47 eV increases slightly superlinearly. This implies that the centers responsible for the blue emission are saturated. As in Ref. 5, we have observed the bleaching of the blue luminescence with time, as shown in Fig. 2. The decrease of the intensity is nonexponential with two characteristic regions: a fast decrease during the first few seconds with a rate proportional to the excitation density and a slow decrease lasting for hours which appears independent of the excitation intensity. We have observed such bleaching

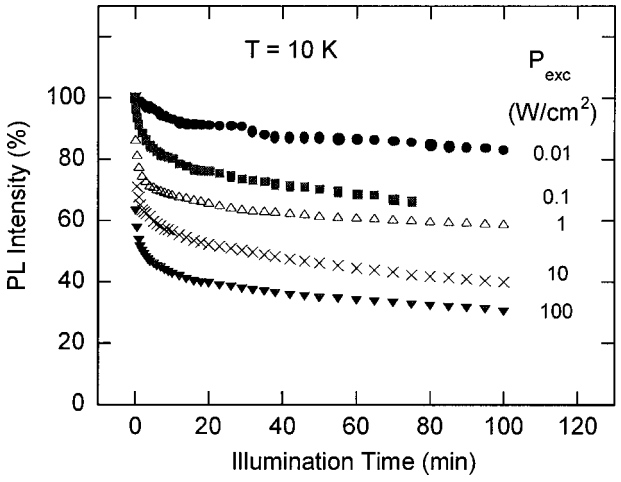

FIG. 2. Variation of the blue-band intensity with time (recorded at 2.8 eV). The intensity at ''zero time '' is normalized to 100% for all excitation densities. The bleaching with time has fast and slow components. The latter is nearly independent of the excitation density.

of the blue band in all the etched samples. It should be noted that the intensity of the exciton emission and other PL bands did not vary with time under the same conditions. This rules out the possibility that bleaching is caused by heating of the sample by the laser beam.

The observed bleaching of the blue-band intensity, more pronounced under high-excitation densities, is irreversible at low temperatures, yet it can be restored to its original value by heating the sample in vacuum. When the sample was illuminated at an excitation density of about 10 W/cm^2 (the diameter of the beam spot was about 0.3 mm) for several hours at 10 K, the blue-band intensity dropped about three times. Mapping of the sample confirmed that the PL from the illuminated spot is reduced about three times compared to the rest of the sample. After keeping the sample in the dark for 1 h at 10 K, the PL intensity from the illuminated spot remained unchanged. However after keeping the sample for 30 min at 100 and 200 K, the intensity increased 1.5 times and practically reached the original value, respectively.

With increasing temperature from 10 to 120 K, the blue PL at a low-excitation density quenched four times and the intensity decrease could be well fitted by a standard equation with the activation energy of 12 meV (Fig. 3). At higher temperatures the intensity decreased faster (activation energy was about 100 meV), so that up to room temperature the signal drops about 100 times. Notice that in this sample both the exciton-related emission and the green band quickly quenched in the temperature range of interest so that their contribution to the blue luminescence at 2.8 eV remained negligible at all temperatures studied.[15]

We suggest that the GaN surface oxidizes in air, resulting in a bandbending caused by the charge localized at the surface states, which are distributed in the lower part of the gap, as shown in the schematic diagram depicted in Fig. 4. Photogenerated electrons can be captured by shallow donors and the holes can be efficiently captured by the surface states since the latter are confined near the surface by the bandbending. An increase of the radiative recombination at the surface indicates that postetching oxidation causes a change in the distribution of the surface states or in the nature of the

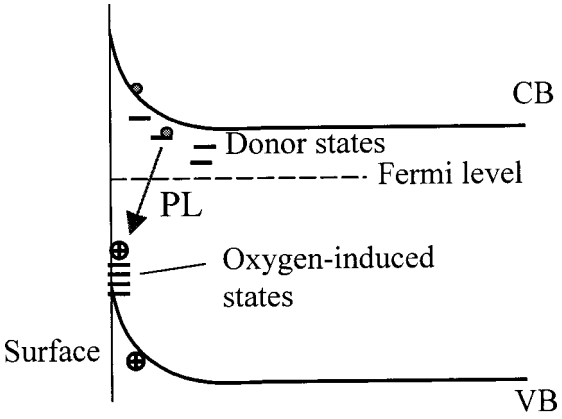

FIG. 4. Proposed model of the blue luminescence in the etched GaN.

local surface bonds. The relatively high quantum efficiency of the blue luminescence may be related to the large hole-capture cross section of the radiative surface states or to the confinement effect. The blueshift of the blue band with increasing excitation density can be explained by reduction of the bandbending at high-excitation levels so that transitions become more vertical. The quenching of the PL intensity below 120 K with activation energy of about 12 meV may be due to release of captured electrons from the shallow donor states. We tentatively attribute the subsequent quenching with the activation energy of about 100 meV to the thermal escape of the electrons bound to a deeper donor below the conduction band.

Various models could explain the observed evolution of the bleaching effect under high-excitation levels. At first glance, it looks unlikely that desorption of oxygen atoms, which may be assisted by illumination, is responsible for this effect since the intensity can be restored in vacuum by increasing the temperature. However, the PL restoration could be due to the surface migration of the absorbed atoms at elevated temperatures. An alternative explanation is that the surface states have a metastable character and illumination causes redistribution between the radiative and nonradiative states of the same defect at the surface. We assume that the previously reported blue band, which emerged after dry etching,[5] is also related to the surface states, and its bleaching with time at the high-excitation level has an origin similar to ours. Further investigations are necessary to elucidate the mechanism of the PL bleaching. It must be emphasized that the origin of the blue band studied in this work should be different from that of the blue band (with the maximum at 2.88 eV) often observed in metal–organic vapor-phase deposition grown undoped GaN samples.[16] Indeed, the position, shape, and behavior versus temperature and excitation intensity are very different for these two PL bands.

In summary, we have observed a blue band in the PL spectrum of GaN epitaxial layers after light etching in hot H_3PO_4. We have attributed the presence of the blue band in the etched samples to the subsequent oxidation of the GaN surface. At low temperatures the radiative recombination is rather efficient. The blue luminescence irreversibly bleaches with time at low temperatures. We tentatively relate the irreversible bleaching to the oxygen desorption or the metastable nature of the surface defects. The origin of the blue band, and its blueshift with increasing excitation intensity and thermal quenching with low activation energy, have been explained in a model whereby transitions from the shallow donors (or conduction band) in the near-surface region to the surface states take place.

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